

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

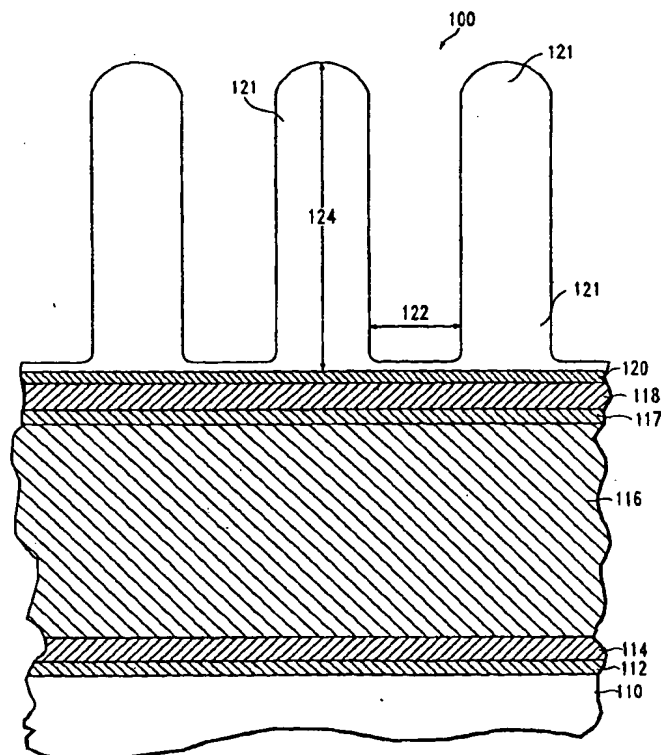
PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : H01L 21/027, 21/3213	A1	(11) International Publication Number: WO 99/30357 (43) International Publication Date: 17 June 1999 (17.06.99)
(21) International Application Number: PCT/US98/25817 (22) International Filing Date: 4 December 1998 (04.12.98) (30) Priority Data: 08/986,911 8 December 1997 (08.12.97) US (71) Applicant: APPLIED MATERIALS, INC. [US/US]; 3050 Bowers Avenue, Santa Clara, CA 95054 (US). (72) Inventors: IONOV, Pavel; 941 Tamarack Lane #1, Sunnyvale, CA 94087 (US). KIM, Sung, Ho; 2298 Lemoyne Way, Campbell, CA 95008 (US). LI, Dean; 5th floor, No. 197, Sec. 2 Ting-Chou Road, Taipei (TW). (74) Agents: BERNADICOU, Michael, A. et al.; Blakely, Sokoloff, Taylor & Zafman LLP, 7th floor, 12400 Wilshire Boulevard, Los Angeles, CA 90025 (US).	(81) Designated States: JP, KR, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>	

(54) Title: METHOD FOR ETCHING SILICON OXYNITRIDE AND INORGANIC ANTIREFLECTION COATINGS**(57) Abstract**

The present disclosure pertains to a method for plasma etching a semiconductor patterning stack (100). The patterning stack includes at least one layer comprising either a dielectric-comprising antireflective material (120) or an oxygen-comprising material (120). In many instances the dielectric-comprising antireflective material (120) will be an oxygen-comprising material, but it need not be limited to such materials. In one preferred embodiment of the method, the chemistry enables the plasma etching of both a layer of the dielectric-comprising antireflective material (120) or oxygen-comprising material and an adjacent or underlying layer (118) of material. In another preferred embodiment of the method, the layer of dielectric-comprising antireflective material (120) or oxygen-comprising material is etched using one chemistry, while the adjacent or underlying layer (118) is etched using another chemistry, but in the same process chamber. Of particular interest is silicon oxynitride, an oxygen-comprising material which functions as an antireflective material. A preferred embodiment of the method provides for the use of a source of carbon and an appropriate halogen-comprising plasma, to achieve selective etch of one oxygen-containing material compared with another material which contains a more limited amount of oxygen.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

METHOD FOR ETCHING SILICON OXYNITRIDE
AND INORGANIC ANTIREFLECTION COATINGS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention pertains to a method of etching silicon oxynitride and other oxygen containing materials. In addition, the method is applicable to inorganic antireflective coating (ARC) materials. Silicon oxynitride is commonly used as an antireflective coating in combination with deep ultraviolet (DUV) photoresists.

2. Brief Description of the Background Art

In the field of semiconductor device fabrication, DUV photoresists have been developed which take advantage of shorter wavelengths of ultraviolet radiation to enable the patterning of smaller-dimensioned electronic and optical devices than possible with traditional, or so called I-line photoresists.. Generally, the photoresist is applied over a stack of layers of various materials to be patterned in subsequent processing steps. Some of the layers in the stack are consumed during the process of patterning underlying layers which become part of the functioning device. To take advantage of the spacial resolution of the photoresist, it is necessary to use an anti-reflective coating (ARC) layer underlying the photoresist, to suppress reflection off other layers in the stack during photoresist exposure. Thus, the ARC layer enables patterning of the photoresist to provide an accurate pattern replication.

Though the most commonly used ARC material is titanium nitride, a number of other materials have been suggested for use in combination with DUV photoresists. For example, U. S. Patent No. 5,441,914 issued August 15, 1995 to Taft et al. describes the use of a silicon nitride anti-reflective layer, while U. S. Patent No. 5,525,542, issued June 11, 1996 to Maniar et al. discloses the use of an aluminum nitride anti-reflective layer. U. S. Patent No. 5,539,249 of Roman et al., issued July

23, 1996, describes the use of an antireflective layer of silicon-rich silicon nitride. U. S. Patent No. 5,635,338 to Joshi et al., issued June 3, 1997, describes a class of silicon-containing materials which display particular sensitivity in the ultraviolet and deep ultraviolet for the formation of patterns by radiation induced conversion into glassy compounds. Joshi et al. recommend the use of anti-reflective coatings such as amorphous silicon and an organic plasma polymerized anti-reflective coating generated from cycloheptatriene. U. S. Patent No. 5,633,210 to Yang et al., issued May 27, 1997 discloses the use of an anti-reflective coating material selected from titanium nitride materials, silicon oxide materials, and silicon oxynitride materials.

Recently there has been increased interest in the use of silicon oxynitride as an anti-reflective coating, due to its ability to function well in combination with DUV photoresist. Silicon oxynitride typically (but not by way of limitation) has a formula of $\text{SiO}_x\text{N}_y\text{H}_z$, where x ranges from 0 to about 2, y ranges from 0 to about 1, and z ranges from 0 to about 1. By changing the composition of the silicon oxynitride ARC layer, one can control reflection onto the photoresist during imaging of the photoresist layer. When $\text{SiO}_x\text{N}_y\text{H}_z$ is used as an ARC, x, y, and z typically range between about 0.2 and about 0.5.

Silicon oxynitride as an ARC enables efficient suppression of the reflection from underlying layers while providing superior chemical properties which prevent an undesirable effect in photoresist patterning known as photoresist poisoning. Photoresist poisoning refers to reaction of the surface underlying the photoresist with moisture to form amino basic groups (NH_2^-) which react with the photogenerated acid which is responsible for the photoresist development. Deactivation of the acid by the amino groups is believed to be responsible for formation of the "foot" (widening of the photoresist line just above the substrate) on some ARC materials such as titanium nitride.

The present invention addresses details of the application of dry etch

techniques for pattern transfer into a silicon oxynitride layer. However, the concepts developed for dry etch of a silicon oxynitride layer have application to the dry etch of other oxygen containing substrates.

With reference to a silicon oxynitride layer used as a anti-reflective coating, in such an application, a typical stack of materials for pattern transfer would include: A substrate, which is a dielectric layer used to separate a metal interconnect layer (to be patterned on plasma etching of the etch stack) from underlying device layers. A barrier layer, which prevents the diffusion of material between a conductive layer and the substrate. A conductive layer, which is typically aluminum or an alloy thereof. An anti-reflective-coating (ARC) layer that reduces reflection back into the photoresist during its exposure in the lithography step and allows for better pattern reproduction. And, a photoresist layer which is imaged to provide the pattern for transfer to underlying layers.

It would, then, be desirable to have a dry, plasma-based etch process for transfer of the pattern from the developed photoresist through all of the layers within the complete etch stack, including an ARC layer, a conductive layer, and a barrier layer. Etching of a metal-comprising stack is traditionally achieved in a metal etch chamber using etch stacks with ARC layers such as titanium nitride. However, as silicon oxynitride is a dielectric material, its patterning is traditionally reserved for dielectric etch chambers, and moving the substrate from one process chamber to another, lowers the productivity of the whole process.

The present invention details a method permitting the etch of a dielectric comprising ARC layer such as a silicon-oxynitride ARC in the same chamber as is used for etching the rest of the metal-comprising stack. We have developed a plasma etch process which provides adequate selectivity for a silicon oxynitride ARC layer over organic-based photoresists. In addition, we have obtained a good etch rate for a silicon oxynitride ARC layer while providing excellent pattern transfer through the

ARC layer and other layers of a six layer metal-comprising stack.

SUMMARY OF THE INVENTION

The present invention pertains to a method for plasma etching a semiconductor patterning stack. The patterning stack includes at least one layer comprising either a dielectric-comprising antireflective material or an oxygen-comprising material. In many instances the dielectric-comprising antireflective material will be an oxygen-comprising material, but it need not be limited to such materials. In one preferred embodiment of the method, the chemistry enables the plasma etching of both a layer of the dielectric-comprising antireflective material or oxygen-comprising material and an adjacent or underlying layer of material. In another preferred embodiment of the method, the layer of dielectric-comprising antireflective material or oxygen-comprising material is etched using one chemistry, while the adjacent or underlying layer is etched using another chemistry, but in the same process chamber. Of particular interest is silicon oxynitride, an oxygen-comprising material which functions as an antireflective material.

A preferred embodiment of the method provides for the use of a source of carbon and an appropriate halogen-comprising plasma, to achieve selective etch of one oxygen-containing material compared with another material which contains a more limited amount of oxygen.

In a highly preferred embodiment of the invention, a film of silicon oxynitride is plasma etched, and better selectivity is achieved relative to a film of a lower oxygen content material, such as a photoresist, by using fluorine comprising plasma. Preferably the fluorine comprising plasma also comprises a source of carbon. Example of materials which provide both fluorine and carbon include fluorocarbons such as CHF_3 , CF_4 , CF_3Cl , C_2F_4 , C_2F_6 and combinations thereof. The fluorocarbons may be combined with other gases which increase the halogen content of the plasma,

such as Cl_2 , F_2 , HIF , HCl , NF_3 , or SF_6 , for example, but not by way of limitation. The addition of such other gases is helpful in increasing the etch rate, and in some instances the selectivity, of the silicon oxynitride. When the gas used to increase the halogen content comprises a halogen other than fluorine, such as chlorine, the etch rate of some other stack layer materials such as a TiN_x barrier layer is also increased. The addition of chlorine to a fluorocarbon plasma should enhance etch of such a barrier layer material along with the silicon oxynitride, while the etch of an oxygen-poor material such as a photoresist is suppressed.

We have discovered a preferred combination of plasma etch gases which provides an unexpectedly high etch rate while providing selectivity for silicon oxynitride over patterning photoresist. The preferred combination of plasma etch gases is CHF_3 and Cl_2 , wherein the gas flow ratio of CHF_3 to Cl_2 ranges between about 2 : 1 and about 1 : 3, wherein a ratio of about 2 : 1 is recommended for high silicon oxynitride to photoresist selectivity, and a higher chlorine content is recommended for etching both the layer of silicon oxynitride and an underlying layer containing a metal or a refractory metal such as titanium nitride. It is expected that the use of CF_4 rather than CHF_3 would require less Cl_2 to selectively etch silicon oxynitride and that CF_4 alone might be sufficient. Further, since the silicon etch rate is dependent on fluorine rather than chlorine, the use of CF_4 should increase the etch rate of silicon oxynitride and may provide an improvement in selectivity as compared with CHF_3 .

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a schematic of the cross-sectional view the preferred embodiment metal etch stack incorporating silicon oxynitride as the ARC layer.

Figures 2A - 2D illustrate the Example One stack cross-sectional view

schematic as the etch stack shown in Figure 1 progresses through a three step etch process.

Figures 3A - 3C illustrate the Example Two stack cross-sectional view schematic as the etch stack shown in Figure 1 progresses through a two step etch process, including one step for etching the silicon oxynitride and titanium nitride layers and a second metal etch step for etching the three layers as described with reference to figure 2C.

Figure 4 shows a plasma processing apparatus of the kind used in carrying out the etching processes described herein.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

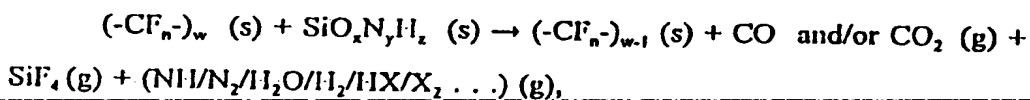
A method is disclosed for the selective etching of silicon oxynitride and other oxygen-comprising layers on a multilayered substrate. The method provides for the selective etching of such oxygen-comprising substrates in a halocarbon-comprising etch plasma, and particularly in a fluorocarbon-comprising etch plasma. Finally, an especially preferred embodiment for the selective etching of silicon oxynitride is described.

Polymer films derived from carbon and halogens which are present in an etch plasma have been observed to deposit on the surfaces of silicon and silicon oxide during etch processing, see for example, S. Arai et al., Japanese J. of Appl. Phys., Part 1, V. 31, 2011-2019 (1992).

We wanted to use silicon oxynitride as an anti-reflective coating in a multi-layered etch structure for the plasma etching of an aluminum conductive layer. To etch the silicon oxynitride we used a fluorocarbon-comprising plasma. Although we were not certain that polymer films were depositing on substrate surfaces during the

etching of the silicon oxynitride, we suspected this might be the case. During development of the etching process, we discovered that we could adjust the selectivity of the etch for silicon oxynitride compared to the photoresist used to pattern the multi-layered etch structure (stack) by adjusting the atomic ratio of fluorine to carbon in the gases supplied to the process chamber.

It appears that the selectivity of silicon oxynitride etch is improved through the formation of a fluorine-comprising polymer. We believe that while the polymer builds up on the surfaces of non-oxygenated materials, slowing down etching on these surfaces, on the surface of silicon oxynitride, the following reaction takes place:



where $(-CF_n-)_{\text{w}}$ is the polymer layer.

This reaction results in consumption of the polymer simultaneously with etching of silicon oxynitride, while producing highly volatile byproducts. These byproducts are later removed as exhaust with the help of a vacuum pump.

To maximize the selectivity of the etch, the proper balance of carbon and fluorine in the plasma is achieved by adjusting the flow rates of gases injected into the etch processing chamber. Such adjustment is usually made by selecting from the following options: Choosing the primary gas feed with a particular carbon to fluorine atomic ratio, where the ratio may be adjusted by selection from gases such as CHF_3 , CF_4 , C_2F_4 , C_2F_6 or a combination thereof; adding oxygen or another oxidizing agent which binds with carbon in the plasma to suppress the formation of polymer; and adding a gas which serves as a source of carbon, such as CO , when it is desired to increase the polymer formation. It should be mentioned that if photoresist is present in the etch chamber, its erosion during the plasma etching process produces considerable amounts of carbon, and the composition of the gas feed has to be adjusted in conjunction with the pattern density of the photoresist and possible with

the kind of photoresist.

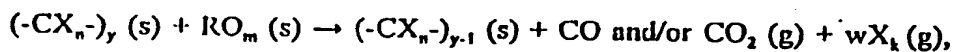
We have achieved a surprising increase in the etch rate of silicon oxynitride by adding an assisting halogen-comprising gas such as Cl_2 , F_2 , HF , HCl , or SF_6 (preferably Cl_2 and SF_6) to the fluorocarbon-comprising plasma feed gases. This list of gases can be extended to include other gases which serve as a source of halogen atoms in the plasma. The benefits of using such an assisting gas are twofold. If etching of silicon oxynitride is carried out in a metal etch chamber, and this is desirable when the silicon oxynitride is used as an ARC layer in a metal stack, such halogen-containing gases are likely to be connected to the etch system for the purpose of metal etch. Also, the addition of a halogen other than fluorine appears to provide additional flexibility in controlling the etch rates of other materials exposed to the plasma. For example, the etching of a titanium nitride barrier layer is better using chlorine than fluorine, and the addition of chlorine to a fluorocarbon-comprising plasma enhances the etching of this material simultaneously with the etching of silicon oxynitride, while the etching of an adjacent photoresist is suppressed due to the presence of polymer or halocarbon species on its surface.

We have discovered a preferred combination of plasma etch gases which provides an unexpectedly high etch rate while providing selectivity for silicon oxynitride over patterning photoresist. The preferred combination of plasma etch gases is CHF_3 and Cl_2 , wherein the gas flow ratio of CHF_3 to Cl_2 ranges between about 2 : 1 and about 1 : 3, wherein a ratio of about 2 : 1 is recommended for high silicon oxynitride to photoresist selectivity, and a higher chlorine content is recommended for simultaneous etching of silicon oxynitride and a barrier layer such as titanium nitride. It is expected that the use of CF_4 rather than CHF_3 would require less Cl_2 to selectively etch silicon oxynitride and that CF_4 alone is likely to be sufficient. Further, since the silicon etch rate is dependent on fluorine rather than chlorine, the use of CF_4 should increase the etch rate of silicon oxynitride and may

provide an improvement in selectivity as compared with CHF_3 .

In view of the successful etching of silicon oxynitride, we believe that in a halocarbon-based etch plasma it is possible to improve the selectivity of oxygen-comprising layers over adjacent layers which contain substantially less oxygen or no oxygen, using the method described above and expanded upon below.

In particular, a carbon source and an appropriate halogen-comprising plasma can be used to achieve selective etching of an oxygen-comprising material compared with a material which contains no oxygen or a substantially reduced amount of oxygen. We believe that the following reaction would take place between an oxygen-rich substrate and a polymer film or halocarbon-comprising species on its surface.



where $(-\text{CX}_n-)_y$ is the polymer layer or halogen-comprising species; X is a halogen, such as F, Cl, Br, or I; RO_m is an oxygen containing material, such as $\text{SiO}_2\text{N}_y\text{H}_z$, SiO_2 , or TiO_2N_y ; $w\text{X}_k$ is the halogenated etch byproduct, such as SiF_4 , TiF_4 , or TiCl_4 ; and (s) and (g) represent a solid and a gas, respectively.

The overall outcome of this reaction is that part of the polymer (or halocarbon-comprising species) reacts with the substrate material to form gaseous products that can be subsequently removed from the plasma process chamber with the exhaust gases. Thus, an oxygen-comprising material is etched while the etching of a material which does not contain oxygen is hindered. By choosing the appropriate halogen so that the halogenated byproducts $w\text{X}_k$ have the highest possible vapor pressure, the best results can be achieved.

1. DEFINITIONS

As a preface to the detailed description, it should be noted that, as used in this specification and the appended claims, the singular forms "a", "an", and "the" include plural referents, unless the context clearly dictates otherwise. Thus, for example, the

term "a semiconductor" includes a variety of different materials which are known to have the behavioral characteristics of a semiconductor, reference to "a conductive material" includes metals such aluminum, copper, platinum, iridium, rubidium, and combinations and alloys thereof, as well as other conductive materials which would be suitable in the application described.

Specific terminology of particular importance to the description of the present invention is defined below.

The term "aluminum" includes alloys of aluminum of the kind typically used in the semiconductor industry. Such alloys include aluminum-copper alloys, and aluminum-copper-silicon alloys, for example. Typically such alloys of aluminum comprise about 0.5 % copper. In addition, as is known in the art, aluminum typically exhibits a surface layer of aluminum oxide.

The term "antireflective coating", "antireflective layer" or "ARC" includes materials which are applied to a surface to reduce its reflection of electromagnetic radiation.

The term "decoupled plasma source" or "DPS" as used herein refers to a plasma etch apparatus with separate controls for the inductive coupling of RF power which controls plasma density (source power) and the bias power which controls ion bombardment energy of the substrate surface.

The term "dielectric ARC" or "dielectric-comprising ARC" refers to an ARC which comprises a dielectric material.

The term "feature" refers to metal lines, trenches and openings in a dielectric layer, and other structures which make up the topography of the substrate surface. Feature size often refers to the size of the smallest feature on the wafer.

The term "ion bombardment" refers to the collision of ions with a surface. The ions are accelerated toward the surface by electric fields in the vicinity of the surface exposed to a plasma.

The term "plasma" refers to a partially ionized gas containing an approximately equal number of positive and negative charges, as well as some other number of non-ionized gas species.

The term "selectivity" is used to refer to a) a ratio of etch rates of two materials; and b) a condition achieved during etch when etch rate of one material is increased in comparison with another material. Note that there are various kinds of materials included in a stack of layers used in an etching process.

The term "source power" refers to the power that is responsible for sustaining the plasma by providing a major portion of the energy to ionize the neutral species in the chamber.

The term "stack" or "etch stack" refers to a collection of layers of different materials deposited one over the other, at least a portion of which are etched during an etching process. A "metal stack" refers to a "stack" which, upon completion of a metal etch process becomes a metal-comprising feature on a substrate.

The term "substrate" includes semiconductor materials, glass, ceramics, polymeric materials, and other materials of use in the semiconductor industry.

The term "vertical profile" refers to a feature profile wherein a cross-section of the feature exhibits side walls which are perpendicular to the surface on which the feature stands. Alternatively, a "positive profile" is one wherein the width of the cross-section of the feature is larger at the surface on which the feature stands than at a distance away from the surface.

II. AN APPARATUS FOR PRACTICING THE INVENTION

The preferred embodiment etch processes described herein were carried out in a Centura® Integrated Processing System available from Applied Materials, Inc. of Santa Clara, California. The system is shown and described in United States Patent No. 5,186,718, the disclosure of which is hereby incorporated by reference. This

equipment included a Decoupled Plasma Source (DPS) of the kind described by Yan Ye et al. at the Proceedings of the Eleventh International Symposium of Plasma Processing, May 7, 1996 and as published in the Electrochemical Society Proceedings, Volume 96-12, pp. 222 - 233 (1996). The plasma processing chamber enables the processing of an 8 inch (200 mm) diameter silicon wafer.

A schematic of the processing chamber is shown in Figure 4 which shows an etching process chamber 410, which is constructed to include at least one inductive coil antenna segment 412 positioned exterior to the etch process chamber 410 and connected to a radio frequency (RF) power generator 418 (source power generator with a frequency tunable around 2 MHz for impedance matching at different plasma conditions). Interior to the process chamber is a substrate 414 support pedestal (cathode) 416 which is connected to an RF frequency power generator 422 (bias power generator of frequency fixed at 13.56 MHz) through an impedance matching network 424, and a conductive chamber wall 430 which serves as the electrical ground 434.

The semiconductor substrate 414 is placed on the support pedestal 416 and gaseous components are fed into the process chamber through entry ports 426. A plasma is ignited in process chamber 410 by applying RF powers 418 and 422. Pressure interior to the etch process chamber 410 is controlled using a vacuum pump (not shown) and a throttle valve 427 situated between process chamber 410 and the vacuum pump. The temperature on the surface of the etch chamber walls is controlled using liquid-containing conduits (not shown) which are located in the walls of the etch chamber 410. The temperature of the semiconductor substrate is controlled by stabilizing the temperature of the support pedestal and flowing helium gas in the channels formed by the back of the substrate and grooves (not shown) on the pedestal 416 surface. The helium gas is used to facilitate heat transfer between the substrate and the pedestal. During the etch process, the substrate surface is

gradually heated by the plasma to a steady state temperature which is approximately 25 - 40 °C higher than the substrate support platen temperature, depending on the process conditions. It is estimated that the substrate surface temperature was typically around 75 °C during most of our experiments. The surface of the etching chamber walls was maintained at about 80 °C using the cooling conduits previously described.

III. EXAMPLES OF ETCHING SILICON OXYNITRIDE

Three sets of experiments were performed. First, the basic effect of etch chemistry was evaluated by etching unpatterned silicon oxynitride and unpatterned I-line photoresist wafers and the etch rates were compared to estimate the selectivity. (The photoresist and silicon oxynitride were not simultaneously present in the plasma.) CHF_3 , Cl_2 , SF_6 , BCl_3 , and combinations thereof were evaluated in this testing. The etch rates obtained are provided in Table I below. The etch conditions were as follows. The plasma source power was 1400 W; the bias power was 130 W; the process chamber pressure was 13 mTorr; the substrate support platen temperature was 45 °C; the support platen back side helium pressure was 10 Torr, with a typical leak of 3 - 6 sccm, and etching was carried out for 40 seconds. This experimentation indicated that CHF_3 and Cl_2 used together provided the most promising combination of selectivity and etch rate.

**Table I: Unpatterned SiO₂N₂ and Photoresist Etch Rates and Selectivity
As A Function of Etch Gas Feed Composition**

Cl ₂ (sccm)	BCl ₃ (sccm)	SF ₆ (sccm)	CHF ₃ (sccm)	SiO ₂ N ₂ ER (Å/min)	PR ER (Å/min)	Select
100	--	--	--	1222	2820	0.443
--	100	--	--	724	643	1.13
--	--	100	--	2625	6048	0.434
--	--	--	50	2112	1467	1.44
50	--	--	50	2884	2512	1.15
--	50	--	50	1789	1564	1.14
--	--	50	50	2713	4575	0.593

where: ER is etch rate; PR is photoresist; and Select is selectivity.

In the second set of experiments, we pattern etched a silicon oxynitride layer of about 3500 Å in thickness which had been applied over a silicon dioxide surface. The pattern was lines and spaces having a feature size down to about 0.25 µm which was transferred from a patterned layer of DUV photoresist (Shipley UV-5 of about 6500 - 7000 Å in thickness). The substrate was then examined with a scanning electron microscope to determine the pattern profile and to estimate the etch rates and selectivity. The details are provided in Tables II and III. It was discovered that, due to the increased amount of carbon released into the plasma from the photoresist surface, silicon oxynitride could not be etched in pure CHF₃ under the process conditions used (basically the same conditions as described above for the initial experimentation). The etch rate had dropped by a factor of about three in the area of the substrate at a distance away from the photoresist lines (open area) and by a factor of about ten in between the lines, as compared to the etch rate of unpatterned silicon oxynitride. This situation was subsequently amended by adding Cl₂ to the plasma gas feed. In particular, the Cl₂ added made up from about 33% to about 75 % of the total volumetric gas flow.

Table II: Process Conditions For The Pattern Etch Of Silicon oxynitride.

Substrate Number	ClIF, /Cl, /BCl, (sccm)	Pressure (mTorr)	Source Power (W)	Bias Power (W)	Bias Temp. (°C)	Time (sec)	Comments
1	50 /0 /0	14	1400	80	45	60	Low etch rate
2	50 /0 /0	12	1400	100	45	180	Low etch rate
3	50 /50 /0	12	1400	100	45	120	Drastic Rate Increase
4	50 /50 /0	12	1400	100	45	60	Looks Good
5	50 /25 /0	12	1400	100	45	60	No Large Change
6	50 / <u>12</u> /0	12	1400	100	45	60	
7	50 /25 /0	12	1400	<u>130</u>	45	<u>45</u>	
8	50 /25 /0	12	1100	100	45	60	
9	50 /25 /0	<u>15</u>	1400	100	45	<u>45</u>	
10	<u>40</u> / <u>20</u> /0	12	1400	100	45	60	
11	50 /25 /0	12	1400	100	<u>30</u>	60	Positive Profile
12	<u>20</u> / <u>20</u> /0	12	1400	100	45	60	Slt. Pos. Profile
13	<u>20</u> / <u>60</u> /0	12	1400	100	45	60	
14	<u>20</u> /0 / <u>60</u>	12	1400	100	45	60	Vry. Pos. Profile

A positive profile is one in which a line is wider at the bottom than at the top, so that the included angle at the base of the line is greater than the desired 90°. Helium backside pressure was 10 Torr throughout all trial runs.

Table III: Etch Rate And Selectivity Of Pattern Etching Silicon oxynitride.
(Substrate numbers correspond with the ones given in Table II)

SUBSTRATE NUMBER	PROCESS CHANGE	ETCH RATE* SiO _x N _y (Å/MIN)	PR LOSS TOP SHOULDER (Å/MIN)	SELECTIVITY** (OPEN/TOP)
5	BASE-LINE	3100	2500 3100	1.2 ± 0.1
6	- Cl ₂	2600	2300 2900	1.1 ± 0.1
7	+BIAS	3450	3300 4200	1.0 ± 0.1
8	- SOURCE	2900	2900 3500	1.0 ± 0.1
9	+ PRESSURE	2900	2700 3400	1.1 ± 0.1
10	- FLOW	2800	2800 3200	1.0 ± 0.1
11	- TEMP	2800	2400 3000	1.2 ± 0.1
12	- FLOW	1700	2500 3400	0.68 ± 0.08
13	- CHF ₃ + Cl ₂	2100	3300 3800	0.64 ± 0.08
14	CHF ₃ + BCl ₃	1300	2000 3100	0.65 ± 0.0

* Etch rate in the open area.

** Ratio of the open area etch rate to the photoresist loss rate at the top in a 0.25µm / 0.25 µm (line/space) line array.

In the third set of experiments, a full metal stack upon a silicon wafer substrate, which included an aluminum metal layer and titanium nitride barrier layers was etched. The profiles were examined with the help of a scanning electron microscope. The details for the third set of experiments are given in the EXAMPLES provided below.

Figure 1 illustrates a typical preferred embodiment etch stack 100 for patterning an aluminum conductive layer to feature sizes down to 0.25 µm or less using a DUV photoresist as a patterning means. In particular, the substrate 110 is a layer of silicon dioxide overlying a silicon wafer surface (not shown). The barrier layer is a bilayer composed of a 300 Å thick layer of titanium 112, followed by a 500 Å thick layer of titanium nitride 114. Overlying titanium nitride barrier layer 114 is a 5,200 Å thick layer 116 of aluminum alloy containing 0.5 % copper.

Overlying aluminum alloy layer 116 is a second 300 Å thick layer of titanium 117, followed by a 500 Å thick layer of titanium nitride 118. Overlying second titanium nitride layer 118 is a layer of silicon oxynitride 120 about 300 Å thick. Overlying silicon oxynitride layer 120 is a layer of patterned DUV photoresist 121, where the pattern is lines and spaces and where the lines and spaces have a varying width 122 of about 0.2 µm and larger, and have a height and a height 124 of about 0.7 µm (7,000 Å). In the preferred embodiments described herein, the DUV photoresist was UV-5, manufactured by Shipley Company of Marlborough, Massachusetts. We also evaluated a DUV photoresist manufactured by Shin-Estu of _____ Japan, which preformed in a similar manner.

EXAMPLE ONE:

This Example is for a three step etch in which the SiO_xN_y ARC layer is etched in Step 1, the underlying TiN and Ti barrier layers are etched in Step 2, with the aluminum alloy layer, and underlying TiN and Ti barrier layers being etched in Step 3. With reference to Figures 2A through 2D, Figure 2A illustrates the schematic cross-sectional profile of the preferred embodiment stack 200 (the same stack as 100 described with reference to Figure 1) during the three etching steps.

Figure 2B shows the schematic of the cross-sectional profile of the etch stack after the first etch step in which the pattern is transferred from DUV photoresist layer 221 through silicon oxynitride layer 220, stopping at the upper surface of second titanium nitride layer 218. The etch conditions used to carry out this first etch step were as follows. The source power was 1400 W; the bias power was 100 W; the process chamber pressure was 12 mTorr; the substrate support platen temperature was about 45 °C; the gas flow rates were 50 sccm of CHF₃/ 25 sccm of Cl₂, and the wafer back side helium pressure was 12 Torr, with a typical leak of 3 - 6 sccm. The etch time period was 5 seconds.

Figure 2C shows the schematic of the cross-sectional profile of the etch stack after the second etch step in which the pattern is transferred through the second titanium nitride layer 218 underlying silicon oxynitride layer 220, stopping at the upper surface of aluminum layer 216. The etch conditions used to carry out this second etch step were the same as in the first step except that the bias power was 50 W, and the gas flow rates were 15 sccm of CHF_3 / 90 sccm of Cl_2 . The etch time period was 12 seconds.

Figure 2D shows the schematic of the cross-sectional profile of the stack after the third etch step in which the pattern is transferred through the aluminum layer 116, the first titanium nitride barrier layer 214, and the first titanium barrier layer 212, stopping with a slight over etch 226 into the top of silicon dioxide layer 210. The etch conditions used to carry out this second etch step were as follows. The plasma source power was 1100 W; the bias power was 130 W; the process chamber pressure was 8 mTorr; the substrate support platen temperature was 45 °C, the gas flow rates were 5 sccm of CHF_3 / 80 sccm of Cl_2 /40 sccm of BCl_3 , and the wafer back side helium pressure was 12 Torr, with a typical leak of 3 - 6 sccm. The etch was carried out for as long as the end point signal at 396 nm (aluminum and titanium lines) was above the background level plus another 10 seconds.

EXAMPLE TWO:

This Example is for a two step etch in which the SiO_xN_y ARC layer and the underlying titanium nitride and titanium barrier layers, are etched in Step 1; and, the aluminum layer, and titanium nitride and titanium layers which underlie the aluminum layer are etched in Step 2. With reference to Figures 3A through 3C, Figure 3A illustrates the schematic cross-sectional profile of the preferred embodiment stack 300 (the same stack as 100 described with reference to Figure 1) for the two etch steps.

Figure 3B shows the schematic of the cross-sectional profile of the etch stack

after the first etch step in which the pattern is transferred from DUV photoresist layer 321 through silicon oxynitride layer 320, second titanium nitride barrier layer 318, and second titanium layer 317, stopping at the upper surface of aluminum layer 316. The etch conditions used to carry out this first etch step were as follows. The source power was 1400 W; the bias power was 70 W; the process chamber pressure was 12 mTorr; the substrate support platen temperature was 45 °C, the gas flow rates were 20 sccm of CHF_3 / 60 sccm of Cl_2 , and the wafer back side helium pressure was 12 Torr, with a typical leak of about 3 - 6 sccm. The etch time period was 20 seconds. The increased concentration of chlorine, as compared with Example 1, sacrifices the selectivity of silicon oxynitride etch, thus allowing etching of other materials such as titanium nitride. Considering the small thickness of the silicon oxynitride layer, the overall loss of photoresist thickness is negligible and is well justified by the simplification in the etch process.

Figure 3C shows the schematic of the cross-sectional profile of the stack after the second etch step in which the pattern is transferred through aluminum layer 316, first titanium nitride layer 314 and first titanium layer 312, stopping with a slight over etch 326 into silicon dioxide layer 310. The etch conditions used to carry out this second etch step were as follows. The plasma source power was 1000 W; the bias power was 130 W; the process chamber pressure was 8 mTorr; the substrate support platen temperature was 45 °C, the gas volumetric flow rates were 5 sccm of CHF_3 / 80 sccm of Cl_2 / 40 sccm of BCl_3 , and the wafer back side helium pressure was 12 Torr, with a typical leak of 3 - 6 sccm. The etch was carried out for as long as the end point signal at 396 nm (aluminum and titanium lines) was above the background level plus another 10 seconds.

The above described preferred embodiments are not intended to limit the scope of the present invention, as one skilled in the art can, in view of the present disclosure expand such embodiments to correspond with the subject matter of the invention

WO 99/30357

PCT/US98/25817

claimed below.

CLAIMS

We claim:

- 1. A method for plasma etching at least one layer of a dielectric-comprising ARC material in a semiconductor patterning stack, the method comprising: using at least one fluorine-comprising etchant gas, alone or in combination with a chlorine-comprising etchant gas, in a manner which provides selectivity for the ARC dielectric material.**
- 2. The method of Claim 1, wherein said fluorine-comprising gas and said chlorine comprising gas are used in combination with a carbon-comprising gas.**
- 3. The method of Claim 1, wherein said fluorine-comprising gas further comprises carbon.**
- 4. The method of Claim 1, wherein both said dielectric-comprising ARC material and at least one other layer which makes up said semiconductor patterning stack are etched using the same etchant gas or combination of etchant gases.**
- 5. The method of Claim 1, wherein both said dielectric-comprising ARC material and at least one other layer which makes up said semiconductor patterning stack are etched in the same process chamber.**
- 6. The method of Claim 5, wherein said process chamber includes an apparatus which enables independent control of a plasma density and of a source of bias power**

which affects an ion bombardment energy upon a surface of said patterning stack.

7. A method for plasma etching at least one layer of an oxygen-comprising ARC material in a semiconductor patterning stack, the method comprising: using at least one fluorine-comprising etchant gas, alone or in combination with a carbon-comprising gas, in a manner which provides selectivity for the oxygen-comprising material.
8. The method of Claim 7, wherein said fluorine-comprising gas further comprises carbon.
9. The method of Claim 7, wherein both said oxygen-comprising ARC material and at least one other layer which makes up said semiconductor patterning stack are etched using the same etchant gas or combination of etchant gases.
10. The method of Claim 7, wherein both said oxygen-comprising ARC material and at least one other layer which makes up said semiconductor patterning stack are etched in the same process chamber.
11. The method of Claim 10, wherein said process chamber includes an apparatus which enables independent control of a plasma density and of a source of bias power which affects an ion bombardment energy upon a surface of said patterning stack.
12. A method for plasma etching an oxygen-comprising layer in a semiconductor plasma etch patterning stack, comprising: using at least one halogen-comprising etchant gas alone or in combination with other etchant gases, in a manner which provides selectivity for an exposed patterning stack layer containing a higher

percentage of oxygen.

13. The method of Claim 12, wherein said halogen-comprising etchant gas forms a halogen-comprising polymer or species which deposits on surfaces adjacent to said oxygen-comprising layer in an amount sufficient to reduce the etch rate of said adjacent surfaces while permitting the etching of a surface of said oxygen comprising layer, and wherein said oxygen-comprising layer comprises at least three elements or comprises two elements where neither of the two elements is silicon.

14. The method of Claim 12 or Claim 13, wherein said oxygen-comprising layer is silicon oxynitride.

15. The method of Claim 14, wherein said silicon oxynitride is $\text{SiO}_x\text{N}_y\text{H}_z$, where x ranges from 0 to about 2, y ranges from about 0 to about 1, and z ranges from 0 to about 1.

16. The method of Claim 15, wherein x, y, and z range between about 0.2 and about 0.5.

17. The method of Claim 13, wherein said oxygen-comprising layer includes silicon oxynitride and said adjacent surface comprises a photoresist.

18. The method of Claim 17, wherein said photoresist is a DUV photoresist.

19. The method of Claim 12, or Claim 13, wherein said plasma etching is carried out in an apparatus which enables independent control of a plasma density and of a source of bias power which affects an ion bombardment energy of a substrate surface.

20. The method of Claim 14, wherein said plasma etching is carried out in an apparatus which enables independent control of a plasma density and of a source of bias power which affects an ion bombardment energy of a substrate surface.
21. The method of Claim 19, wherein plasma-generated ions are directed toward a surface said oxygen-comprising layer in a manner which activates oxygen contained on said layer surface to react with carbon adjacent to or in contact with said surface.
22. The method of Claim 12, or Claim 13, wherein said halogen-comprising gas is a fluorine-comprising gas.
23. The method of Claim 22, wherein said fluorine-comprising gas is used in combination with a carbon-comprising gas.
24. The method of Claim 22, wherein said fluorine-comprising gas further comprises carbon.
25. The method of Claim 12 or Claim 13, wherein said halogen-comprising etch gas includes an assisting gas which is used to improve the selectivity of said oxygen-comprising layer.
26. The method of Claim 25, wherein said assisting gas is selected from the group consisting of Cl_2 , F_2 , HF , HCl , NF_3 , SF_6 , and combinations thereof.
27. The method of Claim 24, wherein said fluorine-comprising gas is selected from

the group consisting of CHF_3 , CF_4 , CF_3Cl , C_2F_4 , C_2F_6 , and combinations thereof.

28. The method of Claim 27, wherein said fluorine-comprising gas is CHF_3 , CF_4 , or a combination thereof.

29. The method of Claim 27, wherein said assisting gas is selected from the group consisting of Cl_2 , F_2 , HF , HCl , NF_3 , SF_6 , and combinations thereof.

30. The method of Claim 29, wherein said assisting gas is chlorine, and wherein volumetric flow rate of said fluorine-comprising gas to said chlorine ranges between about 2 : 1 and about 1 : 3.

31. A method for plasma etching a silicon oxynitride-comprising layer in a semiconductor plasma etch patterning stack, comprising: using at least one halogen-comprising etchant gas alone or in combination with other etchant gases, wherein said halogen-comprising etchant gas forms a halogen-comprising polymer or species which deposits on surfaces adjacent to said silicon oxynitride-comprising layer in an amount sufficient to reduce the etch rate of said adjacent surfaces while permitting the etching of a surface of said silicon oxynitride-comprising layer.

32. The method of Claim 31, wherein said surface adjacent said silicon oxynitride-comprising layer comprises a photoresist.

33. The method of Claim 32, wherein said photoresist is a DUV photoresist.

34. The method of Claim 31, or Claim 32, or Claim 33, wherein said plasma etching is carried out in an apparatus which enables independent control of a plasma density

and of a source of bias power which affects an ion bombardment energy of a substrate surface.

35. The method of Claim 31, or Claim 31, or Claim 33, wherein said halogen-comprising gas is a fluorine-comprising gas.

36. The method of Claim 35, wherein said fluorine-comprising gas is selected from the group consisting of CHF₃, CF₄, CF₃Cl, C₂F₄, C₂F₆, and combinations thereof.

37. The method of Claim 35, wherein said plasma etch gas includes an assisting gas selected from the group consisting of Cl₂, F₂, HF, HCl, NF₃, SF₆ and combinations thereof, which is used to control the deposition of said fluorine-comprising polymer or species on said stack surface.

38. The method of Claim 37, wherein said assisting gas is chlorine, and wherein volumetric flow rate of said fluorine-comprising gas to said chlorine ranges between about 2 : 1 and about 1 : 3.

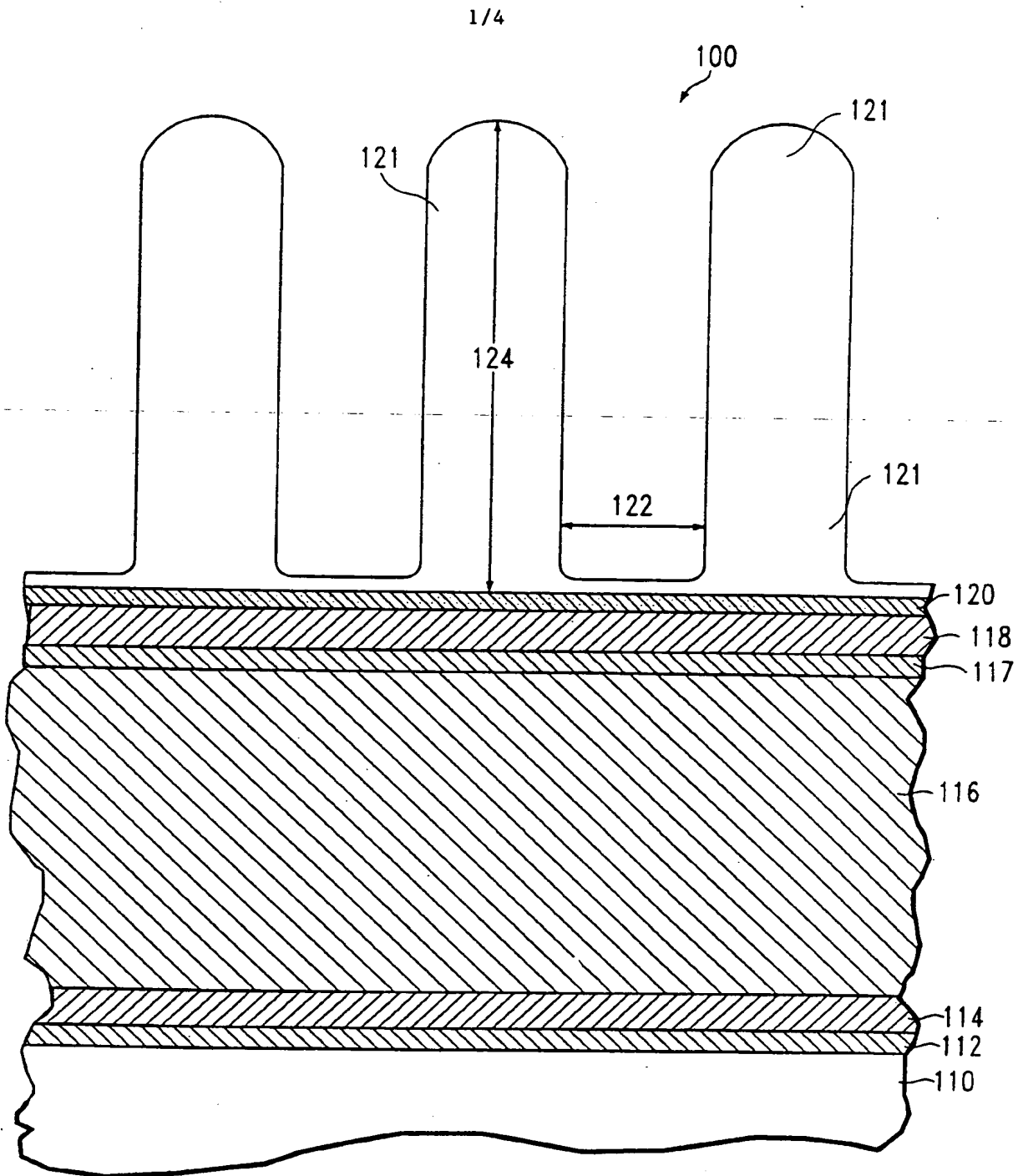
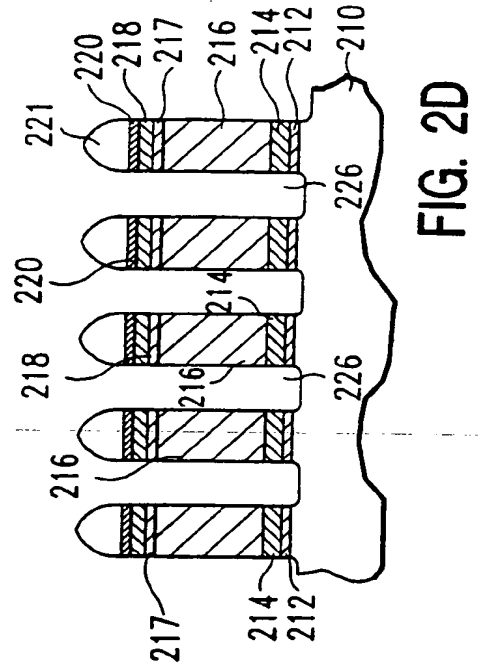
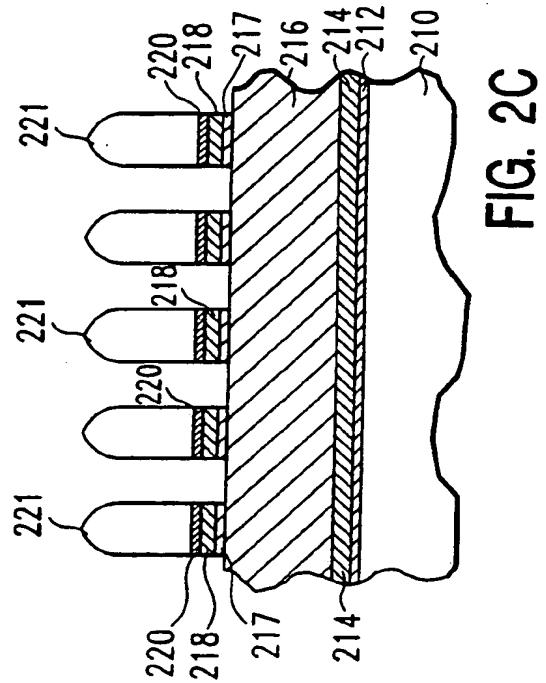
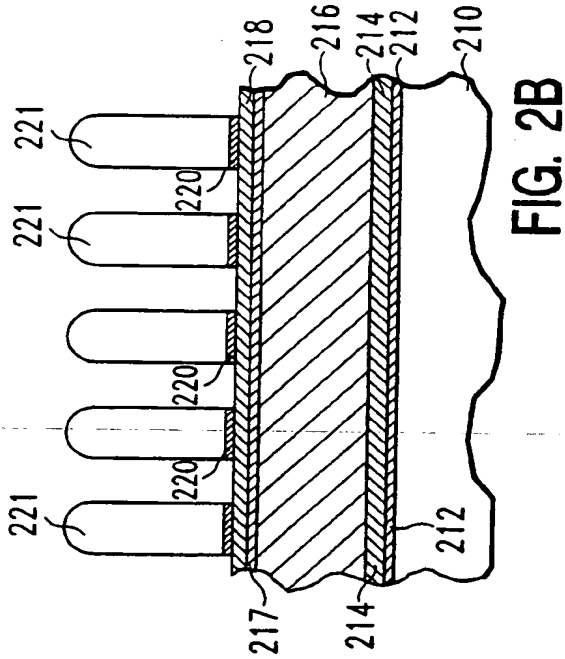
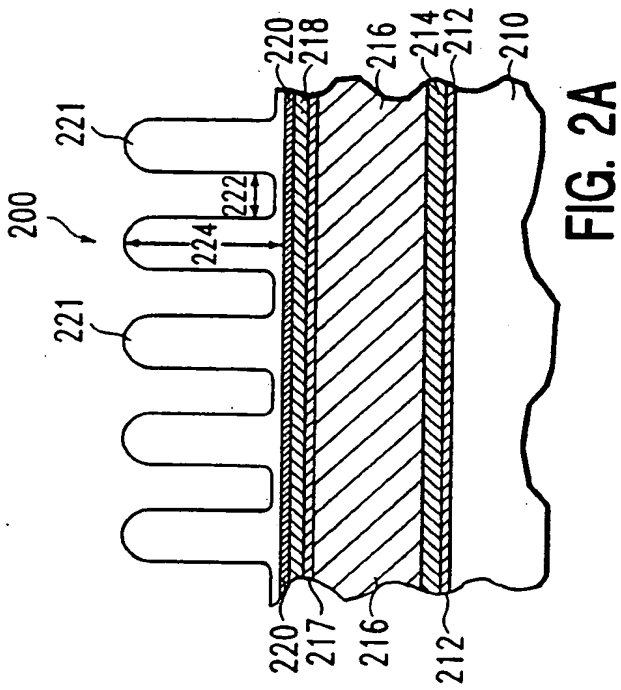


FIG. 1

2/4



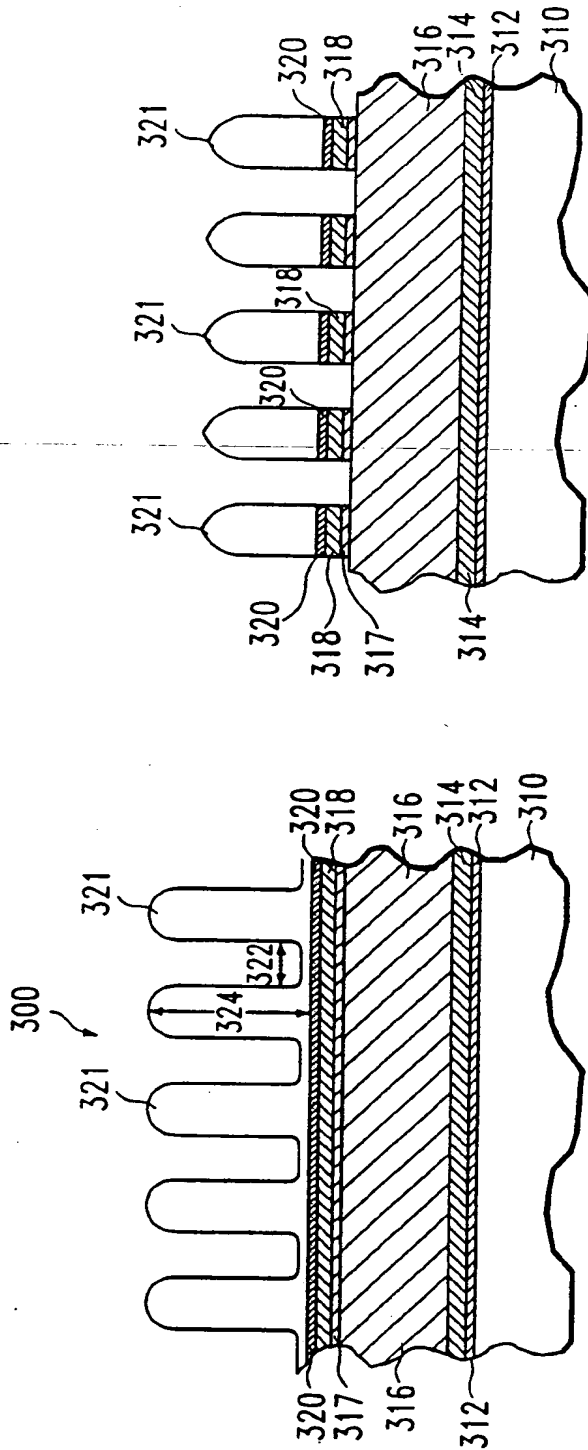


FIG. 3A

FIG. 3B

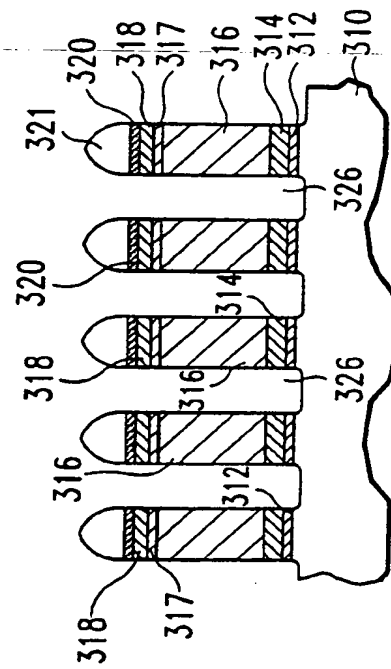


FIG. 3C

4/4

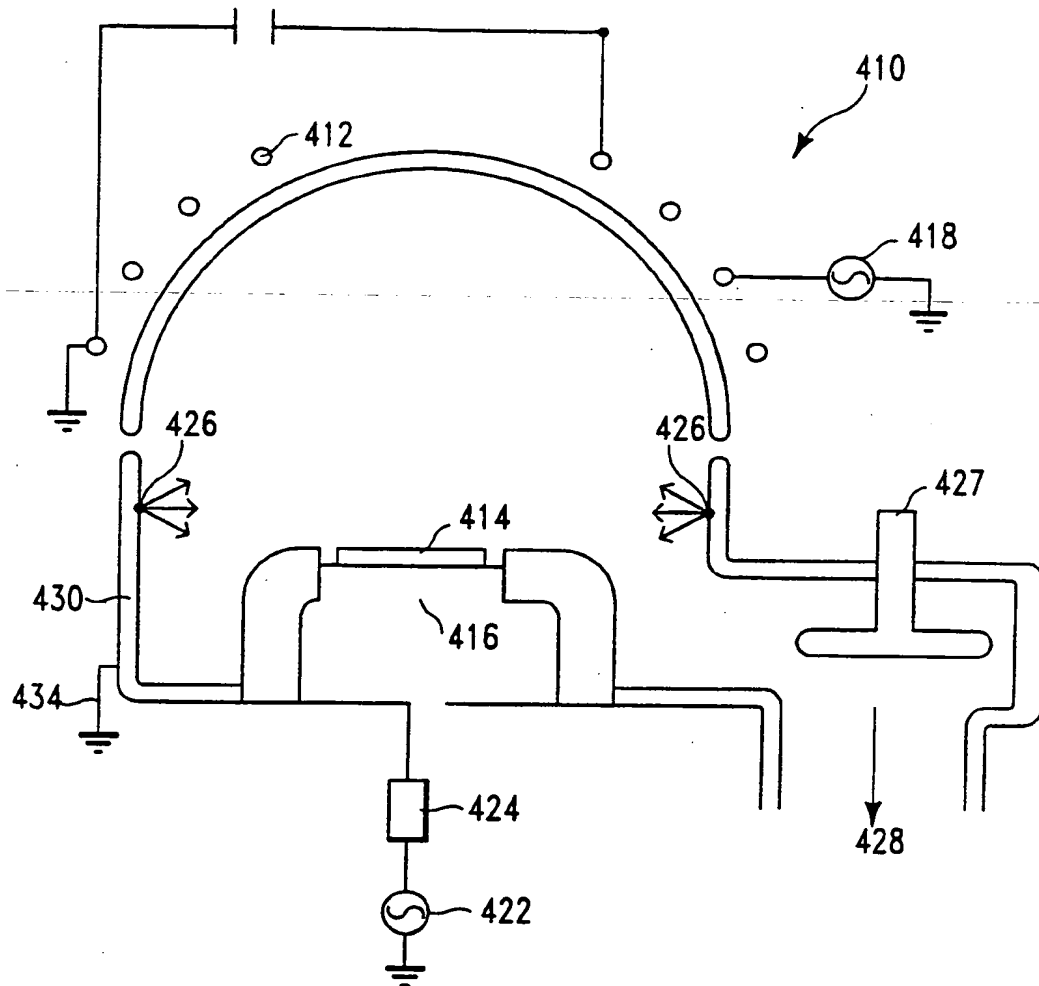


FIG. 4 (PRIOR ART)

INTERNATIONAL SEARCH REPORT

Int. onal Application No
PCT/US 98/25817

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01L21/027 H01L21/3213

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 644 582 A (SONY CORP) 22 March 1995	1-3,7,8, 12-15, 17, 22-24,27
A	see page 5, line 49 - page 6, line 19	21,31, 35,36
X	WO 97 17725 A (ADVANCED MICRO DEVICES INC) 15 May 1997	1-3,7,8, 12-15, 17, 22-24, 27,28
A	see page 5, line 5 - page 17, line 19	25,26, 31,32, 35-37
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

*** Special categories of cited documents :**

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

15 March 1999

Date of mailing of the international search report

29/03/1999

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Schuermans, N

INTERNATIONAL SEARCH REPORT

Int. onal Application No

PCT/US 98/25817

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 470 707 A (AMERICAN TELEPHONE & TELEGRAPH) 12 February 1992 see column 2, line 39 - column 4, line 8 ----	1-5, 7-10,12
A	LEE W.W. ET AL: "FABRICATION OF 0.06 MICRONS POLY-SI GATE USING DUV LITHOGRAPHY WITH DESIGNED SixOyNz FILM AS AN ARC AND HARDMASK" PROCEEDINGS OF 1997 SYMPOSIUM ON VLSI TECHNOLOGY, KYOTO, JAPAN, 10 - 12 June 1997, pages 131-132, XP002096577 see page 131, column 1, paragraph 3 - column 2, paragraph 3 ----	1,7,17, 18,32,33
A	Y.YE ET AL.: "0.35 MICRON AND SUB-0.035 MICRON METAL STACK ETCH IN A DPS CHAMBER - DPS CHAMBER AND PROCESS CHARACTERIZATION" PROCEEDINGS OF THE ELEVENTH INTERNATIONAL SYMPOSIUM ON PLASMA PROCESSING, 5 - 10 May 1996, pages 222-233, XP002096578 LOS ANGELES, CA USA cited in the application see page 222, paragraph 1 ----	6,11,19, 20,34
A	US 5 441 914 A (GUNDERSON CRAIG D ET AL) 15 August 1995 cited in the application see column 3, line 20 - column 4, line 11 -----	1-5,7-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/25817

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0644582	A	22-03-1995	JP 7086244 A	31-03-1995
			DE 69416225 D	11-03-1999
WO 9717725	A	15-05-1997	US 5767018 A	16-06-1998
			EP 0804804 A	05-11-1997
EP 0470707	A	12-02-1992	US 5126289 A	30-06-1992
			DE 69127792 D	06-11-1997
			DE 69127792 T	09-04-1998
			JP 2719465 B	25-02-1998
			JP 4254327 A	09-09-1992
US 5441914	A	15-08-1995	US 5872385 A	16-02-1999